Supporting information

Synergistic Crosslinking and Cage-Structured POSS Integrated in Polyimides: Toward Ultra-Low Dielectric Constant and High-Resolution Photolithography

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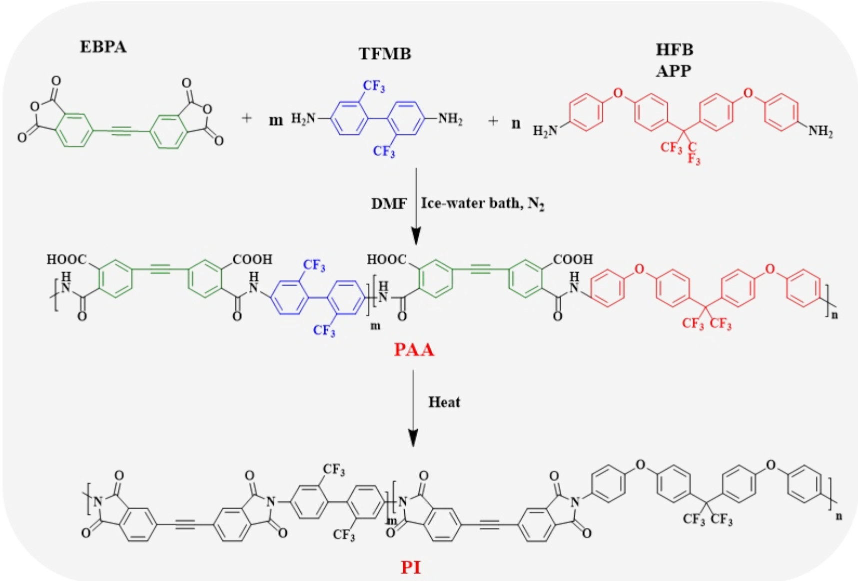

Scheme S1. Synthesis of the fluorinated polyimide films.

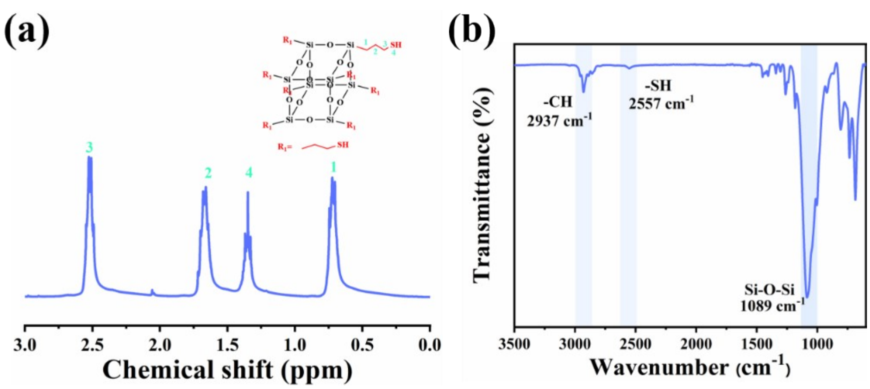

Figure S1. (a) ^{1}H NMR (400 MHz, $CDCl_3$, δ): 0.78 (double, Si-CH_2-), 1.4 (br, -SH), 1.72 (s, -CH_2-), 2.58 (s, -CH_2-S); (b) FTIR of POSS-SH.

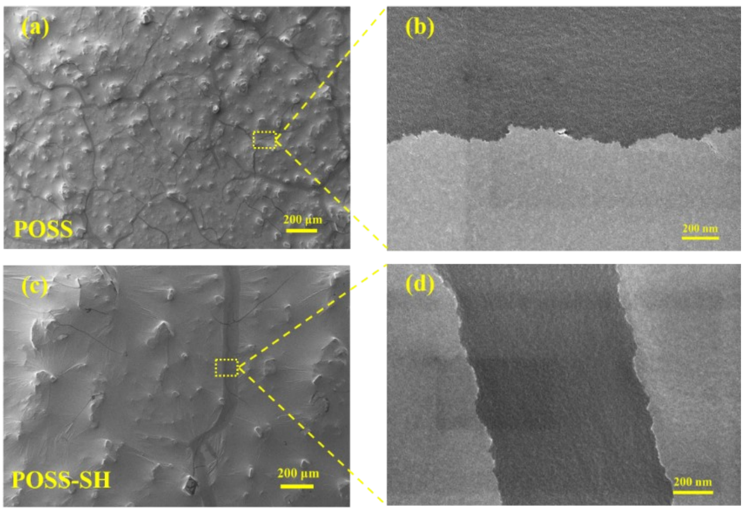

Figure S2. Morphologies of the POSS (a-b) and POSS-SH (c-d)

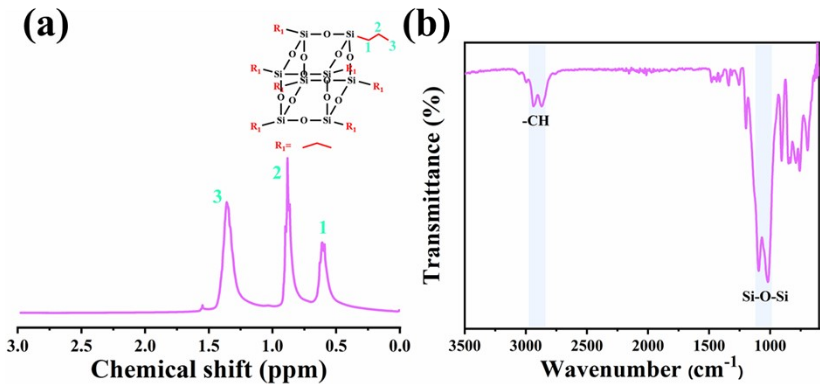

Figure S3. (a) ^{1}H NMR (400 MHz, $CDCl_3$, δ): 0.62 (double, Si-CH_2-), 0.87 (s, -CH_2-), 1.35 (s, -CH_3); (b) FTIR of POSS.

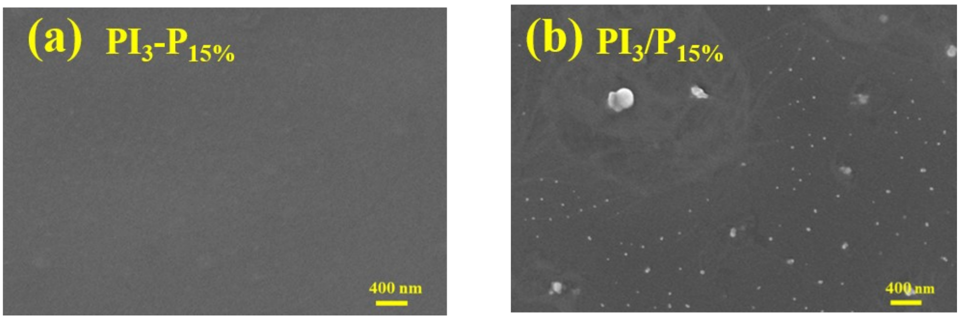

Figure S4. SEM images of (a) covalently crosslinked PI_3-$P_{15\%}$ and (b) physically blended $PI_3/P_{15\%}$.

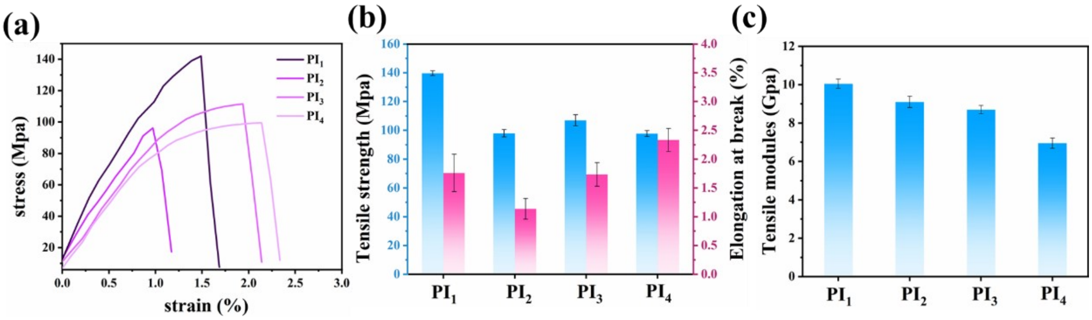

Figure S5. Tensile stress-strain curves of the PI films: (a) Stress-strain behavior of PI_{1-4} films; (b) Tensile strength (MPa) and elongation at break (%) of the PI_{1-4} films; (c) Elastic modulus (GPa) of the PI_{1-4} films.

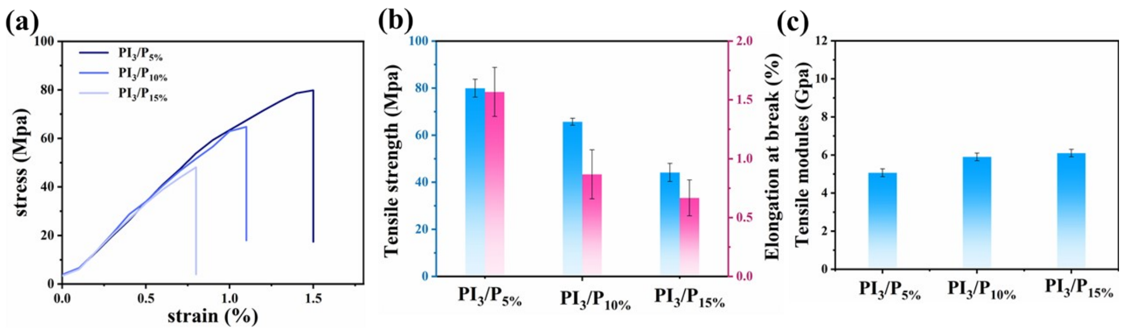

Figure S6. (a) Tensile stress-strain curves of the PI_3/P films; (b) Tensile strength and Elongation at break and (c) elastic modulus.

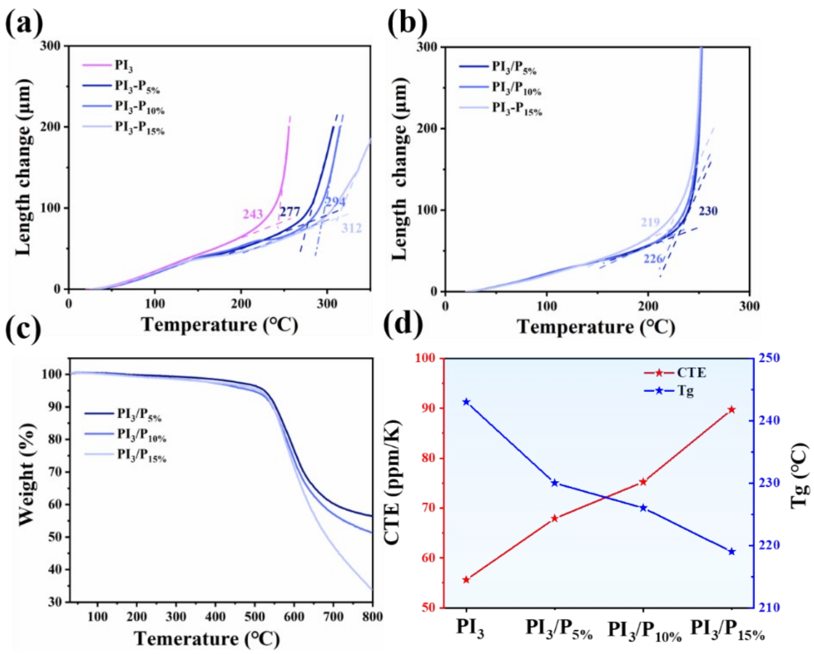

Figure S7. TMA curves of (a) PI-P and (b) PI/P; (c) TGA curves of PI/P and (d) CTE (30-200 °C) and T_g measured by TMA curves for PI/P films.

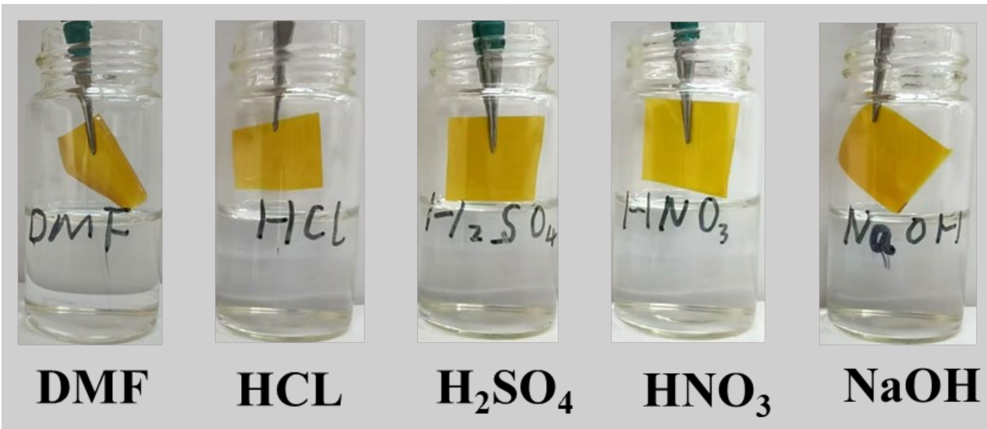

Figure S8. Solubility of PI_3-$P_{15\%}$ films after 30 days (DMF was chosen as an example for photographing the organic solvents.)

Table S1 The D_k, D_f and the patterning resolution of the reported photosensitive polyimides.

Sample name	Maximum resolution (μm)	D_k	D_f	Ref
PI_3-$P_{15\%}$	7	2.21 (10 Ghz)	0.0029 (10 Ghz)	This work
PSPI-2	10	3.16 (5 Ghz)	0.0098 (5 Ghz)	1
n-PSPI-2	7	2.73 (10 Ghz)	0.0032 (10 Ghz)	2
n-LTPI-IMZ-2.0	5	2.8 (10 Ghz)	0.0058 (10 Ghz)	3
QL-FGQDs/PI	3	2.65 (1 MHz)	0.009 (1 Mhz)	4
PI-$PyF_{5\%}$-200	3	3.18 (10 Ghz)	0.00241 (10 Ghz)	5
C-PI-3	5	2.93 (10 Ghz)	0.0096 (10 Ghz)	6

Table S2. Mechanical and thermal properties of the resulting PI_3-P films

	Thermal properties			Mechanical properties					
	TGA			DSC	TMA				
Samples	$T_{d,5\%}$ [°C]	$T_{d,30\%}$ [°C]	$^{a}T_{HRI,30\%}$ [°C]	$^{b}T_g$	$^{c}T_g$	CTE	σ_{max} [MPa]	ε_b [%]	E [GPa]
PI_3	534	626	316.8	--	243	55.6	104.2	1.7	8.7
PI_3-$P_{5\%}$	528	631	294.9	--	277	51.7	98	1.5	9.6
PI_3-$P_{10\%}$	518	616	282.6	--	294	49.2	104.6	2.4	8.3
PI_3-$P_{15\%}$	506	607	277.6	--	312	45.6	110.2	2.7	8.2

a:$T_{HRI} = 0.49 \times [T_{d,5\%} + 0.6 * (T_{d,30\%} - T_{d,5\%})]$; $T_{d,5\%}$, and $T_{d,30\%}$ were the corresponding decomposition temperatures of 5% and 30% weight loss, respectively.

b : glass transition temperatures according to the DSC measurements;

c: glass transition temperatures according to the TMA measurements

Table S3. Mechanical and thermal properties of the resulting PI_3/P films

	Thermal properties			Mechanical properties					
	TGA			DSC	TMA				
Samples	$T_{d,5\%}$ [°C]	$T_{d,30\%}$ [°C]	$^{a}T_{HRI,30\%}$ [°C]	$^{b}T_g$	$^{c}T_g$	CTE	σ_{max} [MPa]	ε_b [%]	E [GPa]
PI_3	534	626	316.8	--	243	55.6	104.2	1.7	8.7
PI_3/$P_{5\%}$	525	623	286.1	--	230	67.9	79.8	1.6	5.1
PI_3/$P_{10\%}$	511	612	280.1	--	226	75.2	64.6	0.9	5.9
PI_3/$P_{15\%}$	496	605	275.0	--	219	89.7	48.4	0.7	6.1

a: $T_{HRI} = 0.49 \times [T_{d,5\%} + 0.6 * (T_{d,30\%} - T_{d,5\%})]$; $T_{d,5\%}$, and $T_{d,30\%}$ were the corresponding decomposition temperatures of 5% and 30% weight loss, respectively.

b: glass transition temperatures according to the DSC measurements;

c: glass transition temperatures according to the TMA measurements

Reference

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